

5

Rotational Motion

Aims

By the end of this chapter you should be able to:

- Use the one-dimensional Schrödinger equation to derive the wavefunctions for a particle moving in a circle
- Apply the three-dimensional Schrödinger equation to the movement of a particle on the surface of a sphere
- Apply the spherical model to the rotation of diatomic molecules and to electron and nuclear spin

Vector notation. In this chapter we meet vectors for the first time. The velocity, v , is a vector quantity because it has both magnitude and direction. Such vectors will normally be shown in bold face type, and ordinary face type will be reserved for situations where only the magnitude of the vector is required. Thus, v will denote the speed of a particle. The square of a vector is automatically defined as a scalar quantity, being equal to the magnitude of the vector squared, and it will always be shown in ordinary type.

All the systems that we have considered so far have been restricted to motion along a straight line, whereas most of the systems of interest to chemists involve particles circulating around a fixed point, for example electrons circulating around nuclei, molecules rotating about their centre of mass and electrons spinning on their axes. In this chapter we consider those systems in which a particle rotates at a constant distance from a fixed point. In the following chapter this treatment will be extended to the hydrogen atom, where the distance of the electron from the nucleus is variable.

5.1 Circular Motion in a Fixed Plane

We begin with the simplest case in which a particle of mass m moves at a constant speed v around a circle of radius r , as shown in Figure 5.1. The distance moved by the particle along the circumference of the circle from its starting position is denoted by s , and the angle subtended at the centre is denoted by ϕ . It should be noted that s and ϕ are considered to be positive for anti-clockwise motion and negative for clockwise motion. Before obtaining solutions of the Schrödinger equation for this

system, it will be useful to review some basic concepts from classical mechanics.

5.1.1 Classical Treatment

The velocity of the particle at any instant is represented by the vector v . Whilst the magnitude of this vector remains constant, its direction is continually changing as the particle moves around the circle, and it is not a constant of the motion. This difficulty can be overcome by describing the movement in terms of the angular velocity ω , which is numerically equal to the rate of change of the angle ϕ . The angular velocity is a vector which points in a direction at right angles to the plane of motion, and therefore does not change direction as the particle goes around the circle. To distinguish between clockwise and anti-clockwise motion, the vector points up or down according to the right-hand screw rule, which is illustrated in Figure 5.2.

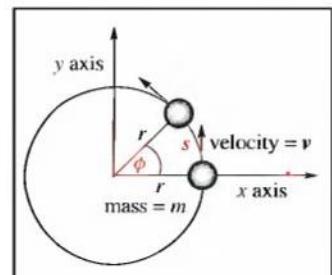


Figure 5.1 Movement of a particle around a circle

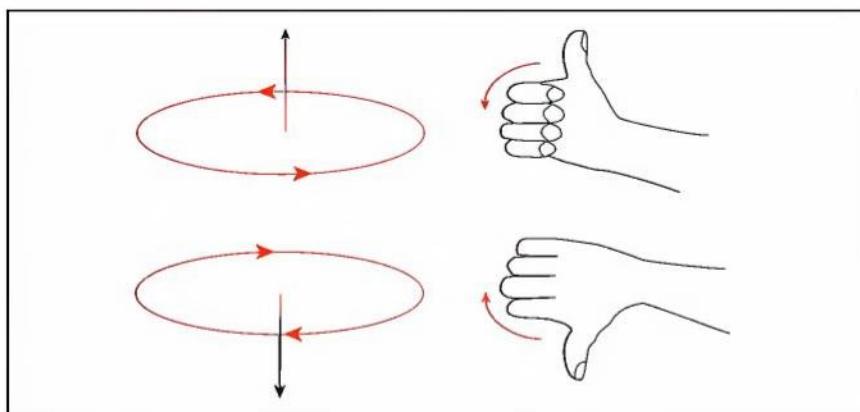


Figure 5.2 The right-hand screw rule for determining the direction of the angular velocity or angular momentum vector

Because $\phi = s/r$ and $ds/dt = v$, it is possible to write the following expression for the magnitude of the angular velocity:

$$\omega = \frac{d\phi}{dt} = \frac{1}{r} \frac{ds}{dt} = \frac{v}{r} \quad (5.1)$$

The kinetic energy of the particle is constant, and equal to $mv^2/2$. In terms of the angular velocity ω , this can be expressed as:

$$E = \frac{1}{2} mr^2 \omega^2 \quad (5.2)$$

The quantity mr^2 is known as the moment of inertia of the particle and is given the symbol I . Thus:

$$E = \frac{1}{2} I \omega^2 \quad (5.3)$$

This equation has the same form as the equation for linear motion, but with moment of inertia and angular velocity substituted for mass and linear velocity, respectively. For rotational motion it is generally true that the angular velocity and the moment of inertia have an analogous role to velocity and mass in linear motion. In keeping with this principle, we can define an angular momentum vector, \mathbf{L} , as follows:

$$\mathbf{L} = \mathbf{I}\omega \quad (5.4)$$

Clearly, this vector has the same directional properties as ω . In terms of \mathbf{L} , equation (5.3) then becomes:

$$E = \frac{\mathbf{L}^2}{2I} \quad (5.5)$$

This equation is equivalent to the equation $E = p^2/2m$ for linear motion. With the substitutions $I = mr^2$ and $\omega = v/r$, the magnitude of the angular momentum can also be written as:

$$\mathbf{L} = mvr \quad (5.6)$$

5.1.2 Quantum Mechanical Treatment

The one-dimensional Schrödinger equation can still be used to describe the motion of the particle if the Cartesian coordinate x is replaced by s , the distance moved by the particle along the circumference of the circle from its starting point. Although this variable describes a curved path, its use in place of x can be justified because the particle is constrained to move along this path. With the potential energy V put equal to zero, the Schrödinger equation can then be written as:

$$-\frac{\hbar^2}{2m} \left(\frac{d^2\psi}{ds^2} \right) = E\psi \quad (5.7)$$

The length of the arc of a circle is equal to the radius of the circle multiplied by the angle subtended at the centre, that is, $s = r\phi$. Thus, $ds = rd\phi$, and equation (5.7) becomes:

$$-\frac{\hbar^2}{2mr^2} \left(\frac{d^2\psi}{d\phi^2} \right) = E\psi \quad (5.8)$$

This equation could have been obtained more rigorously by solving the two-dimensional Schrödinger equation:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \right) = E\psi \quad (5.9)$$

and making the substitutions $x = r\cos\phi$ and $y = r\sin\phi$, but this method involves much more complicated mathematics.

The moment of inertia, I , of the rotating particle is defined by the relation $I = mr^2$. Thus, equation (5.8) can be rewritten as:

$$-\frac{\hbar^2}{2I} \left(\frac{d^2 \psi}{d\phi^2} \right) = E\psi \quad (5.10)$$

From equation (5.5) the energy is equal to $L^2/2I$, where L is the angular momentum of the particle; equation (5.10) can therefore be rearranged to give:

$$-\frac{d^2 \psi}{d\phi^2} = \left(\frac{L}{\hbar} \right)^2 \psi \quad (5.11)$$

Putting $L/\hbar = \alpha$, the solutions of this equation take the form:

$$\psi = N e^{\pm i\alpha\phi} \quad (5.12)$$

where N is a normalization constant.

If the wavefunction is expanded in the form:

$$\psi = N(\cos\alpha\phi \pm i\sin\alpha\phi) \quad (5.13)$$

it can be seen to consist of two sinusoidal waves, one real and the other complex.

Boundary Condition

The boundary condition relevant to motion in a circle is different from that required for a particle in a box, where the wavefunction had to go to zero at the ends of the box. For circular motion the wavefunction has to match up with itself after one complete revolution of the circle. This requires the circumference of the circle to be equal to a whole number of wavelengths. The situation where five wavelengths fit into the circle is illustrated for the sine function in Figure 5.3a. The plot for the cosine function would be similar, but rotated through 90°. If this condition is not met the waves will not coincide with one another after one complete revolution, and multiple values of ψ will be obtained for any particular point on the circle, as shown in Figure 5.3b. As we saw in Section 1.4.5,

It is worth noting that equation (5.10) is identical to the one-dimensional Schrödinger equation for linear motion, except that the Cartesian coordinate x has been replaced by the angle ϕ and the mass has been replaced by the moment of inertia I .

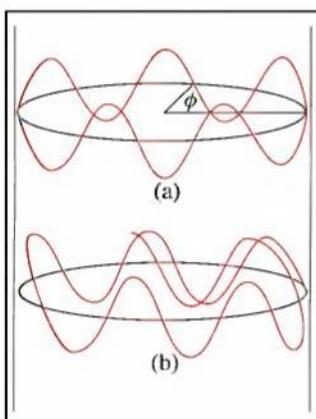


Figure 5.3 Illustration of (a) satisfactory and (b) unsatisfactory wavefunctions. In the first case, five wavelengths fit exactly along the perimeter of the circle, but in the second case there is a mismatch.

satisfactory wavefunctions have to be single-valued, so only wavefunctions of the type illustrated in Figure 5.3a are allowed.

This can be expressed in mathematical terms by stating that the magnitude of the wavefunction must remain the same when the angle ϕ is increased by an amount 2π , that is:

$$\sin \alpha \phi = \sin \alpha(\phi + 2\pi) = \sin(\alpha\phi + \alpha 2\pi) \quad (5.14)$$

and:

$$\cos \alpha \phi = \cos \alpha(\phi + 2\pi) = \cos(\alpha\phi + \alpha 2\pi) \quad (5.15)$$

This will be true only if α is equal to zero or an integer (**quantum number**), which we will call m_l . Thus, acceptable wavefunctions take the form:

$$\psi = N e^{im_l \phi} \quad m_l = 0, \pm 1, \pm 2, \pm 3, \dots \quad (5.16)$$

Positive values of m_l represent anti-clockwise motion, whereas negative values represent clockwise motion. When $m_l = 0$ the particle is stationary. The real (cosine) parts of the wavefunctions for $m_l = 0, \pm 1$ are shown in Figure 5.4. The complex (sine) parts will be similar but rotated through 90° .

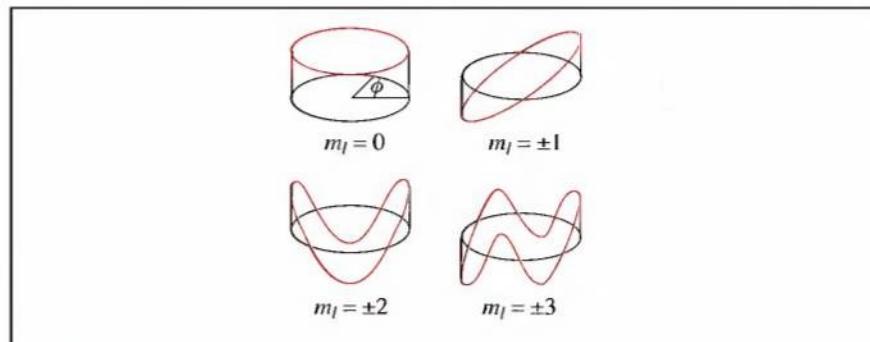


Figure 5.4 The real (cosine) parts of the wavefunction for a particle moving in a circle

Worked Problem 5.1

Q Evaluate the normalization constant N in equation (5.16).

A The probability of finding the particle between ϕ and $\phi + d\phi$ on the circumference of the circle is equal to $\psi^* \psi d\phi$. Since the particle must be somewhere on the circle, the integral of this expression over an angle of 2π must be equal to one. Hence:

$$N^2 \int_{\phi=0}^{\phi=2\pi} e^{-im_l\phi} e^{im_l\phi} d\phi = N^2 \int_{\phi=0}^{\phi=2\pi} d\phi = 1$$

This equation is satisfied when $N = \frac{1}{\sqrt{2\pi}}$. Thus:

$$\psi = \frac{1}{\sqrt{2\pi}} e^{im_l\phi} \quad m_l = 0, \pm 1, \pm 2, \pm 3, \dots \quad (5.17)$$

5.1.3 Quantization of Angular Momentum and Energy

Remembering that $m_l = \alpha = L/\hbar$, we see that the magnitude of the angular momentum of the particle is quantized in units of \hbar , that is:

$$L = m_l \hbar \quad m_l = 0, \pm 1, \pm 2, \pm 3, \dots \quad (5.18)$$

Thus, we come to the important conclusion that the angular momentum of a particle moving at constant speed in a circle can only have values which are multiples of \hbar . This quantization in units of \hbar was first postulated by Niels Bohr in 1913 for the movement of an electron around the hydrogen atom. Later, we shall see that it applies quite generally to the movement of electrons in atoms and molecules.

From equation (5.5) the energy can be expressed as:

$$E = \frac{\hbar^2 m_l^2}{2I} \quad m_l = 0, \pm 1, \pm 2, \pm 3, \dots \quad (5.19)$$

The energy levels are shown in Figure 5.5. It can be seen that, except for the ground state, there are always two states with the same energy, corresponding to clockwise and anti-clockwise movement. Such states are said to be doubly degenerate.

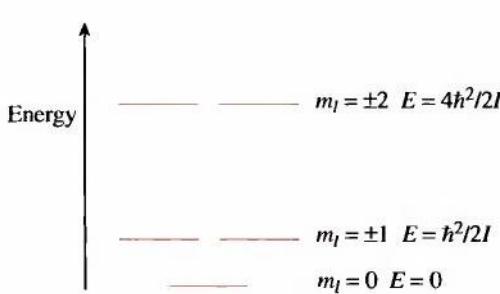


Figure 5.5 The energy levels for a particle moving in a circle

Worked Problem 5.2

Q Use the de Broglie relation to show that the angular momentum of a particle moving in a circle is quantized in units of \hbar .

A Since the circumference of the circular path has to be equal to an integral number of wavelengths, we can write:

$$2\pi r = m_i \lambda$$

where the wavelength is taken to be negative when the particle is moving in a clockwise direction. When this equation is combined with the de Broglie relation, $p = h/\lambda$, the following expression is obtained for the magnitude of the linear momentum at any instant:

$$p = \frac{m_i h}{2\pi r}$$

It can be seen from equation (5.6) that the magnitude of the angular momentum L is equal to mvr , and so to pr . Hence:

$$L = \frac{m_i h}{2\pi} = m_i \hbar$$

5.2 Rotation in Three Dimensions

In this section we consider a particle that is free to move in three dimensions, but always at a constant distance r from a fixed point. In this way, motion is confined to the surface of a sphere, as illustrated in Figure 5.6. The potential energy V is also constant and can be set equal to zero. This model can be applied to the rotation of rigid molecules and also to electron and nuclear spin, as we shall see later. However, the main reason for introducing it at this stage is that it provides a first step towards obtaining mathematical solutions of the Schrödinger equation for the hydrogen atom.

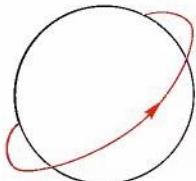


Figure 5.6 Movement of a particle on the surface of sphere

5.2.1 The Schrödinger Equation in Spherical Polar Coordinates

The Schrödinger equation given in Section 4.1 can be extended to three dimensions by writing:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi \quad (5.20)$$

where:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (5.21)$$

∇^2 is known as the Laplacian operator.

This form of the equation is not easily applied to rotational motion because the Cartesian coordinates used do not reflect the centrosymmetric nature of the problem. It is better to express the Schrödinger equation in terms of the spherical polar coordinates r , θ and ϕ , which are shown in Figure 5.7. Their mathematical relationship to x , y and z is given on the left of the diagram. In terms of these coordinates the Laplacian operator ∇^2 becomes:

$$\nabla^2 = \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \Lambda^2 \right] \quad (5.22)$$

where:

$$\Lambda^2 = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (5.23)$$

Although the Schrödinger equation looks much more formidable in spherical polar coordinates than it did in Cartesian coordinates, it is easier to solve because the wavefunctions can often be written as the product of three functions, each one of which involves only one of the variables r , θ and ϕ .

The symbol ∂ indicates differentiation with respect to one variable, while keeping the other two variables constant. This process is known as partial differentiation.

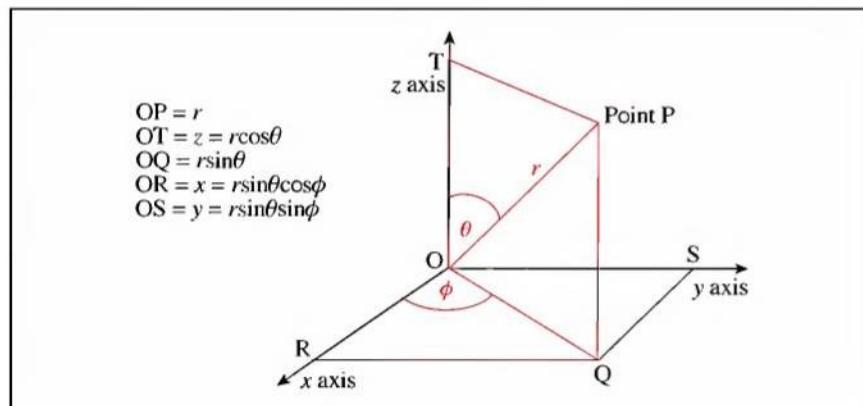


Figure 5.7 The relationship between Cartesian and spherical polar coordinates

Worked Problem 5.3

Q For circular motion in a fixed plane, show that the Laplacian operator given in equations (5.22) and (5.23) leads to the Schrödinger equation derived in Section 5.1.2.

A For a particle moving around a circle in the xy plane, the angle θ is fixed at 90° and r is also a constant. Thus, the differentials with respect to r and θ in equations (5.22) and (5.23) disappear. With $\sin\theta = 1$, the equation for ∇^2 simplifies to:

$$\nabla^2 = \frac{1}{r^2} \frac{d^2}{d\phi^2}$$

With $V = 0$, the Schrödinger equation then becomes:

$$-\frac{\hbar^2}{2mr^2} \frac{d^2\psi}{d\phi^2} = E\psi$$

which is the same as equation (5.8).

5.2.2 Solutions of the Schrödinger Equation for Rotation with Constant r

Because r is a constant, differentiation with respect to r can be ignored in equation (5.22) and the Schrödinger equation in spherical polar coordinates simplifies to:

$$-\frac{\hbar^2}{2mr^2} \Lambda^2\psi = E\psi \quad (5.24)$$

It should be noted that mr^2 is equal to the moment of inertia of the particle, I .

Solutions of this equation take the form:

$$\psi = \Theta(\theta)\Phi(\phi) \quad (5.25)$$

where Θ is a function only of the variable θ , and Φ is a function only of the variable ϕ . The mathematics involved in obtaining the Θ and Φ functions are rather lengthy and only the results will be given here. Those interested in the mathematics should refer to the Appendix at the end of the chapter.

The function Φ is found to be identical to the one already discussed for rotational motion in a fixed plane, that is:

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im_l\phi} \quad m_l = 0, \pm 1, \pm 2, \pm 3 \quad (5.26)$$

The function Θ can take on various forms, depending on the values of two quantum numbers. The first is m_p , and the second is a new quantum number, l , sometimes known as the **azimuthal quantum number**. The latter is restricted to the values $l = 0, 1, 2, 3, \dots$

The modulus of m_l (that is, its magnitude regardless of sign) must never be greater than l . This can be written mathematically as:

$$|m_l| \leq l \quad (5.27)$$

Thus, the allowed values of the two quantum numbers are as follows:

$l = 0$	$m_l = 0$
$l = 1$	$m_l = -1, 0, +1$
$l = 2$	$m_l = -2, -1, 0, +1, +2, \text{etc.}$

The wavefunctions are called **spherical harmonics** because they represent the types of waveform that can be sustained on the surface of a sphere (imagine a tidal wave on a flooded planet), and they are given the symbol $Y_{l,m_l}(\theta, \phi)$ where the subscripts identify the quantum numbers controlling the mathematical form taken by the wavefunctions.

The first few spherical harmonics are shown in Figure 5.8, where only the real parts of the wavefunctions (represented by $\Theta \cos m_l \phi$) have been drawn. With respect to the real parts, the complex parts (represented by $\Theta \sin m_l \phi$) would be rotated by 90° in the xy plane. The lines separating +ve and -ve regions are nodes, points where the real component of the wavefunction is zero. The direction of motion will be at right angles to the nodal lines because this will be the direction in which the wavefunction has maximum curvature. So, for example, the motion for $l = 1$ and $m_l = 0$ will be entirely from one “pole” to the other, with no motion around the “equator”. For $l = 1$ and $m_l = \pm 1$ the motion will be a mixture of movement between the “poles” and around the “equator”. The more nodes that cut the “equator”, the higher is the angular momentum of the particle in the z direction.

Those with some knowledge of chemical bonding will recognize that the spherical harmonics are related to the atomic orbitals, with $l = 0, 1$ and 2 corresponding to s, p and d orbitals, respectively. This subject will be developed further in Chapter 6.

The real parts of the complex wavefunctions can also be regarded as wavefunctions in their own right, because they can be generated by a linear combination of complex wavefunctions with the same energy. Thus:

$$\sin \theta (e^{+i\phi} + e^{-i\phi}) = 2 \sin \theta \cos \phi \quad (5.28)$$

and:

Quantum numbers		$\Theta\Phi$ (normalization constant omitted)	Sign of real part of wavefunction on surface of sphere
l	m_l		
0	0	constant	
1	0	$\cos\theta$	
1	+1	$-\sin\theta e^{i\phi}$	
1	-1	$\sin\theta e^{-i\phi}$	
2	0	$3\cos^2\theta - 1$	
2	+1	$-\cos\theta \sin\theta e^{i\phi}$	
2	-1	$\cos\theta \sin\theta e^{-i\phi}$	
2	+2	$\sin^2\theta e^{2i\phi}$	
2	-2	$\sin^2\theta e^{-2i\phi}$	

Figure 5.8 The first nine spherical harmonic wavefunctions

It should be noted that wavefunctions can be combined in this way only when they have the same energy. Such wavefunctions are said to be degenerate. It is generally true that any linear combination of degenerate wavefunctions will be a solution of the corresponding Schrödinger equation.

$$\sin\theta (e^{+i\phi} - e^{-i\phi}) = 2i \sin\theta \sin\phi \quad (5.29)$$

Polar plots of these real wavefunctions are shown in Figure 5.9 for $l = 0$ and $l = 1$. In these diagrams the distance from the origin is proportional to the magnitude of the wavefunction. It can be seen that the three wavefunctions corresponding to $l = 1$ all have the same dumbbell shape, with positive and negative lobes, but oriented along different Cartesian axes. Once again, those with some knowledge of chemical bonding will recognize these shapes as those of the $2p_x$, $2p_y$ and $2p_z$ atomic orbitals.

5.2.3 Energies of the Wavefunctions

It is shown in the Appendix that the spherical harmonic wavefunctions, Y_{l,m_l} , have the following important property when operated upon by the operator Λ^2 :

$$\Lambda^2 Y_{l,m_l} = -l(l+1) Y_{l,m_l} \quad (5.30)$$

This important equation will now be used to calculate the energies. It

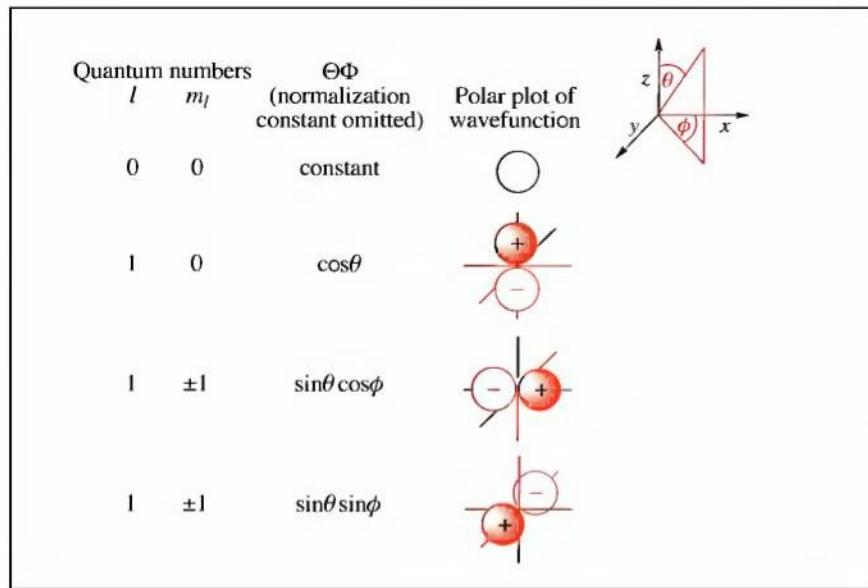


Figure 5.9 Polar plots of the first four spherical harmonic wavefunctions

will also appear in the derivation of the radial wavefunctions for the hydrogen atom.

A combination of equations (5.24) and (5.30) gives:

$$-\frac{\hbar^2}{2mr^2} \nabla^2 Y_{l,m_l} = \frac{\hbar^2}{2mr^2} l(l+1) Y_{l,m_l} = E Y_{l,m_l} \quad (5.31)$$

The function Y_{l,m_l} appears on both sides of this equation and cancels out. From this it follows that the energy of a rotating particle is quantized according to the equation:

$$E = l(l+1) \frac{\hbar^2}{2I} \quad l = 0, 1, 2, 3, \dots \quad (5.32)$$

Because the energy is independent of the value of m_p , there will be $2l + 1$ states with the same energy, and the energy level is said to be **($2l + 1$)-fold degenerate**.

5.2.4 Angular Momentum and Spatial Quantization

The equation relating energy and angular momentum is $E = L^2/2I$ (see equation 5.5). It follows that the angular momentum is quantized, and limited to the following values:

$$L = \sqrt{l(l+1)}\hbar \quad l = 0, 1, 2, 3, \dots \quad (5.33)$$

It should be noted that the function $\Phi(\phi)$, which describes the motion of

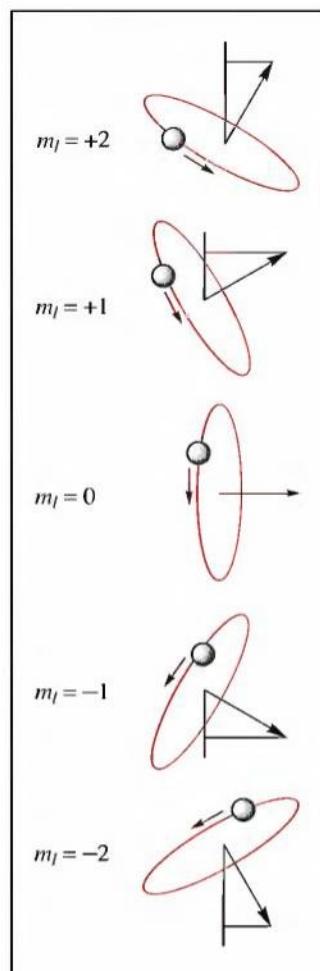


Figure 5.10 The five directions in which the angular momentum vector can point for $l = 2$

the particle in the xy plane, is identical to that for a particle rotating in a fixed plane, for which the angular momentum was found to be equal to $m_l \hbar$. The component of angular momentum directed along the z -axis must therefore be quantized according to the equation:

$$L_z = m_l \hbar \quad m_l = 0, \pm 1, \pm 2, \dots \pm l \quad (5.34)$$

These results can be represented by a vector with a length proportional to $\sqrt{l(l+1)}\hbar$, and oriented so that the projection of the vector on the z -axis is equal to $m_l \hbar$. This is illustrated in Figure 5.10.

For a given value of the quantum number l , there are $(2l + 1)$ directions in which the angular momentum vector can point. If all directions in space are equivalent, the position of the z axis is quite arbitrary, and the $2l + 1$ orientations that the rotating particle can adopt all have the same energy. In the presence of an externally applied electric or magnetic field, however, the z axis is determined by the direction of the field, and the orientation of the angular momentum with respect to this axis will affect the energy.

So far we have discussed the component of the angular momentum in the z direction, but no mention has been made of the components in the x and y directions. The reason for this omission is that the Uncertainty Principle forbids complete knowledge of the orientation of the angular momentum vector. If the component in the z direction is known, then the other two components must remain undetermined. This situation can be represented on a diagram by cones of uncertainty, as shown in Figure 5.11. One end of the angular momentum vector is

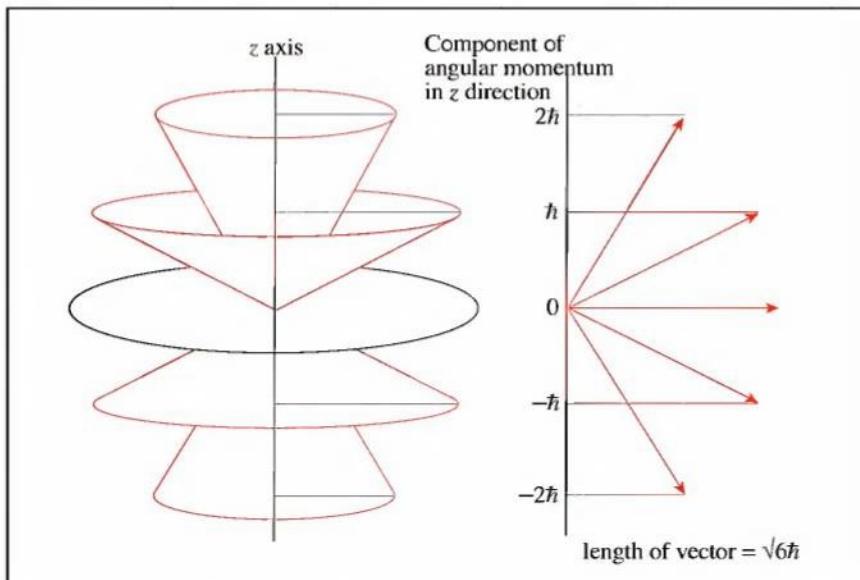


Figure 5.11 The cones of uncertainty on which the angular momentum vectors must lie

considered to be at the apex of the appropriate cone and the other end can then be situated anywhere along the circular cross section at the top of the cone. This concept will be useful when we come to consider electron spins in a later section.

5.2.5 Application to the Rotation of Diatomic Molecules

The rotation of a rigid diatomic molecule about its centre of mass is illustrated in Figure 5.12a. As discussed in Chapter 4, the motion of the two masses, m_1 and m_2 , is mathematically equivalent to the rotation of a single particle of mass μ [$= m_1m_2/(m_1 + m_2)$] about a fixed point, the distance between the point and the particle being equal to the bond length, r . This is illustrated in Figure 5.12b. It is therefore possible to treat the rotation of a diatomic molecule as the motion of a particle of mass μ on the surface of a sphere.

In rotational spectroscopy it is customary to use J as the quantum number, rather than I . With this modification to equation (5.32), the allowed energies of rotation can be written as:

$$E = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2 \dots \quad (5.35)$$

where the moment of inertia $I = \mu r^2$.

For a given rotational energy there will be $(2J + 1)$ possible orientations of the rotating molecule in space, and therefore each rotational state will be $(2J + 1)$ -fold degenerate. Absorption of radiation in the far-infrared region of the spectrum causes molecules to become rotationally excited, the selection rule being that the quantum number J can only increase by one. Thus, the change in rotational energy resulting from the absorption of radiation can be obtained from the equation:

$$\Delta E(J \rightarrow J+1) = \frac{\hbar^2}{2I} [(J+1)(J+2) - J(J+1)] = \frac{\hbar^2}{I} (J+1) \quad (5.36)$$

Worked Problem 5.4

- Q** In the far-infrared spectrum of $^{12}\text{C}^{16}\text{O}$ the rotational transition from $J = 12$ to $J = 13$ causes absorption of radiation at a wavenumber of 50.2 cm^{-1} . For the CO molecule calculate (a) the energy change involved in the transition, (b) the moment of inertia, (c) the reduced mass and (d) the bond length.

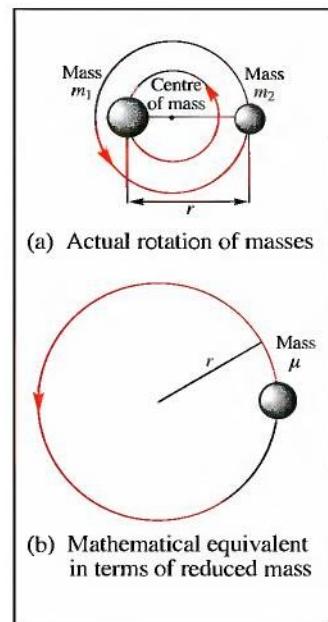


Figure 5.12 The rotation of a diatomic molecule: (a) the actual situation; (b) the equivalent mathematical model used in the calculation

A (a) The energy of the photon absorbed in the transition can be calculated from the equation:

$$E(\text{photon}) = h\nu = \frac{hc}{\lambda}$$

With $1/\lambda = 5.02 \times 10^3 \text{ m}^{-1}$, this becomes:

$$\begin{aligned} E(\text{photon}) &= (6.63 \times 10^{-34} \text{ J s})(5.02 \times 10^3 \text{ m}^{-1})(3.00 \times 10^8 \text{ m s}^{-1}) \\ &= 9.98 \times 10^{-22} \text{ J} \end{aligned}$$

(b) This energy is equal to the difference in rotational energy between the $J = 12$ and the $J = 13$ levels, as obtained from equation (5.36):

$$\Delta E(J = 12 \rightarrow J = 13) = \frac{13\hbar^2}{I}$$

Hence, the moment of inertia can be calculated as follows:

$$I = \frac{13 \times (1.054 \times 10^{-34} \text{ J s})^2}{9.98 \times 10^{-22} \text{ J}} = 1.45 \times 10^{-46} \text{ kg m}^2$$

(c) The reduced mass is obtained from the equation

$$\begin{aligned} \mu &= \left[\left(\frac{12.0 \times 16.0}{12.0 + 16.0} \right) \times 10^{-3} \text{ kg mol}^{-1} \right] \times \left[\frac{1}{6.02 \times 10^{23} \text{ mol}^{-1}} \right] \\ &= 1.14 \times 10^{-26} \text{ kg} \end{aligned}$$

(d) Finally, the bond length is obtained from the formula $I = \mu r^2$. Thus:

$$r = \sqrt{\frac{1.45 \times 10^{-46} \text{ kg m}^2}{1.14 \times 10^{-26} \text{ kg}}} = 1.13 \times 10^{-10} \text{ m}$$

5.3 Spin

Besides the angular momentum resulting from circular motion about a fixed point, many elementary particles have an intrinsic angular momentum which can be considered to arise from the particle spinning on its axis. This spin angular momentum is quantized in much the same way

as the angular momentum of a particle moving over the surface of a sphere.

5.3.1 Electron Spin

The first experiment to demonstrate electron spin was carried out by Otto Stern and Walther Gerlach in 1921, and is illustrated in Figure 5.13. Silver atoms, formed by evaporation from a hot metal source in vacuum, were passed between the poles of an inhomogeneous magnet, and then condensed on to a glass plate. It was found that approximately half of the silver atoms were deflected upwards and half downwards, which resulted in two elongated spots on the detector plate. This observation could be explained only if the silver atoms were behaving like miniature magnets that were able to take up one of two orientations in the magnetic field, as shown in Figure 5.14. Atoms aligned with their south pole uppermost would be deflected upwards because the south pole would be in a stronger magnetic field than the north pole. By the same reasoning, silver atoms with the opposite orientation would be deflected downwards. The magnetic field had to be inhomogeneous, otherwise the forces acting on the north and south poles of the atoms would cancel one another out, and there would be no net deflection.

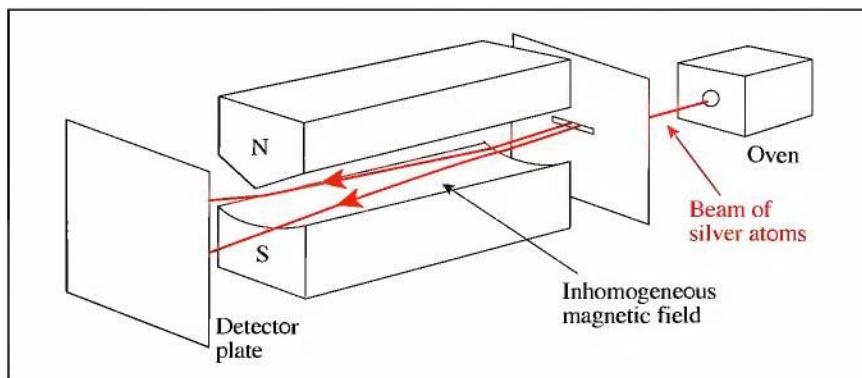


Figure 5.13 The Stern-Gerlach experiment to demonstrate the spin of the electron

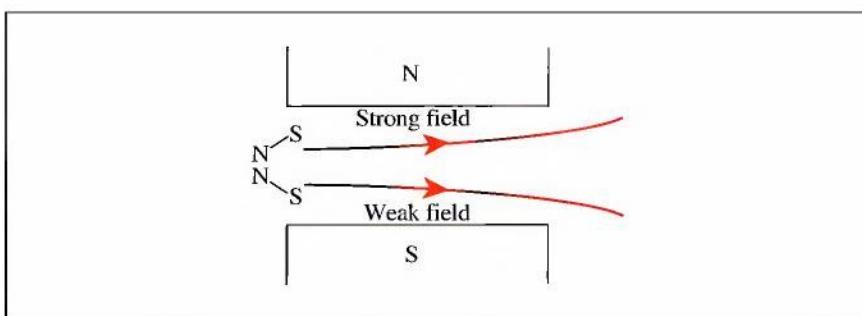


Figure 5.14 The deflection of the silver atoms in the inhomogeneous magnetic field

At the time when the experiments were performed the origin of the magnetic moment on the silver atom was uncertain. It was known from classical physics that an electron undergoing circular motion about an atomic nucleus would have a magnetic moment, but this could not explain the magnetic moment possessed by the silver atom because the single valence electron on the silver atom is in an s orbital, which has no orbital angular momentum. The reason for this will be discussed at length in Chapter 6. Later, it was suggested that the magnetic moment might arise because the valence electron was spinning on its axis, as illustrated in Figure 5.15. It should be emphasized that this is no more than a mental picture of a quantum mechanical phenomenon which has no true classical analogue, but it is a very useful model, provided it is not taken too far.

A spinning particle can be treated mathematically in much the same way as a particle moving on the surface of a sphere. The spin angular momentum vector is denoted by \mathbf{S} and, by analogy with equation (5.33), we expect its magnitude to be given by the equation:

$$S = \hbar \sqrt{s(s+1)} \quad (5.37)$$

where s is the spin angular momentum quantum number (equivalent to l).

The projection of the spin angular momentum vector on to the z axis is denoted as S_z , and, by analogy with equation (5.34), it is restricted to multiples of \hbar given by the equation:

$$S_z = m_s \hbar \quad m_s = s, s-1, s-2, \dots -s \quad (5.38)$$

where m_s is another quantum number (equivalent of m_l). Thus, for a given value of the quantum number s , we expect there to be $2s + 1$ possible orientations of the spin angular momentum vector in the magnetic field. The experiments of Stern and Gerlach show that there are only two orientations that the spinning electron can take up. This requires that s be equal to $\frac{1}{2}$ and that $m_s = \pm \frac{1}{2}$. This is a departure from the conditions for orbiting particles, where the quantum number l was restricted to integral values. The boundary conditions for the electron spin wavefunctions are somewhat different from those for the motion of a particle on the surface of a sphere, and the quantum numbers are therefore subject to different rules. Generalizing from the work of Stern and Gerlach, it can be concluded that all electrons have an intrinsic spin angular momentum, given by the equation:

$$S = \hbar \sqrt{\frac{1}{2} \left(\frac{1}{2} + 1 \right)} = 0.866\hbar \quad (5.39)$$

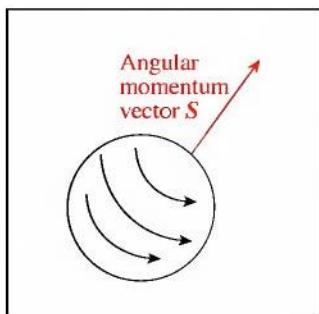


Figure 5.15 A picture of the electron spinning on its axis (not to be taken too literally)

Table 5.1 compares the quantization of angular momenta for both spin and orbital motion.

Table 5.1 Comparison of spin and orbital motion

Orbital motion	Spin
Orbital angular momentum,	Spin angular momentum,
$L = \hbar\sqrt{l(l+1)}$	$S = \hbar\sqrt{s(s+1)}$
Quantum number $l = 0, 1, 2, \dots$	Quantum number $s = \frac{1}{2}$
Component of L in the z direction is restricted as follows: $L_z = m_l \hbar$	Component of S in the z direction is restricted as follows: $S_z = m_s \hbar$
Quantum number $m_l = 0, \pm 1, \pm 2, \dots \pm l$	Quantum number $m_s = \pm \frac{1}{2}$
There are $2l + 1$ possible orientations of the orbital angular momentum for each value of l	There are only two possible orientations for electron spin

Worked Problem 5.5

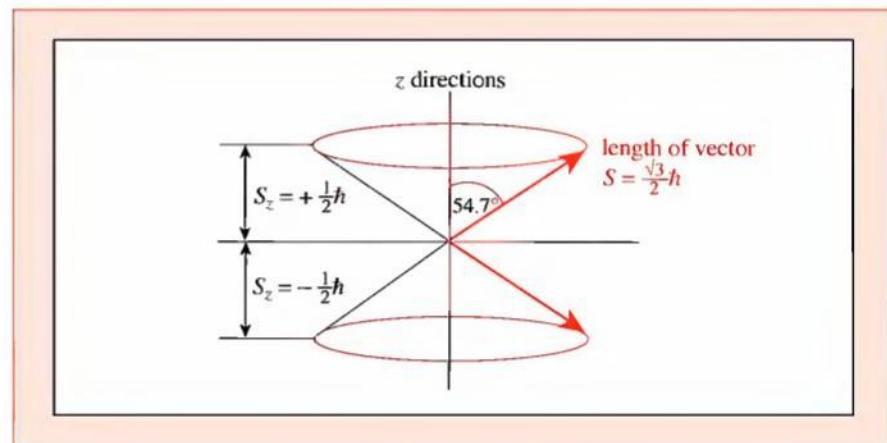
Q For the Stern–Gerlach experiment, calculate the two angles that can be adopted by the spin angular momentum vector of the silver s electron with respect to the direction of the magnetic field.

A The two possible orientations that can be taken up by the spin angular momentum vector are shown in Figure 5.16. For the case where the spin is partially oriented in the direction of the field, the angle θ can be obtained from the equation:

$$\cos \theta = \frac{0.5\hbar}{0.866\hbar} = 0.577$$

Hence $\theta = 54.7^\circ$. When the spin is partially opposed to the field, $\theta = 180 - 54.7 = 125.3^\circ$. Although the angular momentum vector takes up a definite angle with respect to the z axis, its position with respect to the x and y axes remains undefined, and this is represented by the cones of uncertainty in the diagram.

Figure 5.16 The two orientations that can be taken up by the spinning electron



5.3.2 Nuclear Spin of the Proton

Atomic nuclei also have spin, which is quantized in both magnitude and orientation in space. The nuclear spin quantum number is denoted by I , and the magnitude of the angular momentum is equal to $\hbar[I(I + 1)]^{1/2}$.

For the proton, $I = \frac{1}{2}$ and its angular momentum is therefore equal to $0.866\hbar$, which is the same value as that of the electron. However, because the mass of the proton is very much greater than that of the electron, the proton would need to spin much more slowly than the electron if the classical picture of the process is accepted.

In the presence of a magnetic field, the spin angular momentum vector of the proton can take up one of two orientations, just like the electron. This causes two energy levels to be produced, as shown in Figure 5.17. Nuclear magnetic resonance occurs when $\Delta E = h\nu$, where ν is the frequency of the applied radiofrequency field.

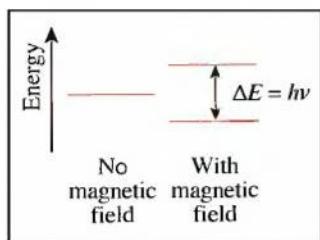


Figure 5.17 The two energy levels that are produced when a proton is placed in a magnetic field

5.3.3 Spins of Other Particles

Other elementary particles also have a characteristic spin. Those with half-integral spin quantum numbers are known as **fermions** and those with integral spin quantum numbers are known as **bosons**. The spin quantum numbers of a variety of particles are given in Table 5.2. When identical particles are interchanged, the wavefunctions associated with fermions and bosons behave differently, and this causes them to have significantly different properties. This will be discussed briefly in Chapter 7, where it is relevant to the way in which electron energy levels in atoms are filled.

Table 5.2 Spin quantum numbers, l , of some fundamental particles

Particle	Fermions Spin quantum number, l	Particle	Bosons Spin quantum number, l
Electron	1/2	Photon	1
Proton (${}^1\text{H}$)	1/2	Deuteron (${}^2\text{H}$)	1
Neutron	1/2	${}^4\text{He}$	0
${}^{13}\text{C}$	1/2	${}^{12}\text{C}$	0
${}^{35}\text{Cl}, {}^{37}\text{Cl}$	3/2	${}^{16}\text{O}$	0

Appendix: Mathematics of Three-dimensional Rotational Motion

The Schrödinger equation for the motion of a particle on the surface of a sphere is:

$$-\frac{\hbar^2}{2I} \Lambda^2 \psi = E\psi \quad (\text{A5.1})$$

where:

$$\Lambda^2 = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \quad (\text{A5.2})$$

We are looking for solutions of the form:

$$\psi = \Theta(\theta)\Phi(\phi) \quad (\text{A5.3})$$

When this expression for ψ is inserted into (A5.1), the equation becomes, after some rearrangement:

$$\frac{\Phi}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2IE}{\hbar^2} \Theta \Phi + \frac{\Theta}{\sin^2 \theta} \frac{d^2 \Phi}{d\phi^2} = 0 \quad (\text{A5.4})$$

Multiplication by $\sin^2 \theta$ and division by $\Theta \Phi$ gives:

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2IE}{\hbar^2} \sin^2 \theta + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = 0 \quad (\text{A5.5})$$

The two variables, θ and ϕ , can now be separated by moving the term in ϕ to the right-hand side:

$$\frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{2IE}{\hbar^2} \sin^2\theta = -\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} \quad (\text{A5.6})$$

Since θ and ϕ can be varied independently of one another, this equation can be satisfied only when both sides of the equation are equal to a constant. Thus:

$$-\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = \text{const.} \quad (\text{A5.7})$$

Assuming that the constant is positive, the solutions of this equation are:

$$\Phi = N e^{i\alpha\phi} \quad (\text{A5.8})$$

where α and N are constants. The constant in equation (A5.7) is then equal to α^2 .

The variable ϕ represents rotation in the xy plane and this type of motion has already been discussed in Section 5.1.2, where satisfactory wavefunctions were found to take the form:

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im_l\phi} \quad \text{with } m_l = 0, \pm 1, \pm 2, \dots \quad (\text{A5.9})$$

This enables α to be equated with m_l , and the constant in equation (A5.7) then becomes m_l^2 . Equation (A5.6) can then be written as:

$$\frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{2IE}{\hbar^2} \sin^2\theta = m_l^2 \quad (\text{A5.10})$$

After division by $\sin^2\theta$ and some rearrangement, this equation becomes:

$$\frac{1}{\Theta \sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) - \frac{m_l^2}{\sin^2\theta} = -\frac{2IE}{\hbar^2} \quad (\text{A5.11})$$

Putting $2IE/\hbar^2$ equal to β , and multiplying throughout by Θ , we obtain:

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) - \frac{\Theta m_l^2}{\sin^2 \theta} + \beta \Theta = 0 \quad (\text{A5.12})$$

Satisfactory solutions of this equation are found only when $\beta = l(l+1)$, where l is a positive integer greater than or equal to the modulus of m_l . Thus, the quantum numbers l and m_l are restricted to the following values:

$$l = 0, 1, 2, 3, \dots \text{ with } |m_l| \leq l.$$

Inserting $\beta = l(l+1)$ and $m_l^2 = -\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2}$ into equation (A5.12) and rearranging, we obtain:

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{\Theta}{\sin^2 \theta} \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -l(l+1)\Theta \quad (\text{A5.13})$$

Multiplying throughout by Φ gives:

$$\frac{\Phi}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{\Theta}{\sin^2 \theta} \frac{d^2\Phi}{d\phi^2} = -l(l+1)\Theta\Phi \quad (\text{A5.14})$$

The left side of this equation is equivalent to $\Lambda^2(\Theta\Phi)$ and therefore:

$$\Lambda^2(\Theta\Phi) = -l(l+1)\Theta\Phi \quad (\text{A5.15})$$

The wavefunctions that satisfy equation (A5.1) are known as spherical harmonics, and they are written as $Y_{l,m_l}(\theta, \phi)$, where l and m_l are the quantum numbers that determine the particular form that the wavefunction takes. With this notation, equation (A5.15) becomes:

$$\Lambda^2 Y_{l,m_l}(\theta, \phi) = -l(l+1) Y_{l,m_l}(\theta, \phi) \quad (\text{A5.16})$$

Summary of Key Points

1. The wavefunction for a particle moving in a circle has been shown to be:

$$\psi = \frac{1}{\sqrt{2\pi}} e^{im_l \phi}$$

where ϕ is the angle of rotation and m_l is a quantum number restricted to the values $0, \pm 1, \pm 2, etc.$. Positive and negative values of m_l represent motion in opposite directions around the circle. The angular momentum of the particle is equal to $m_l \hbar$, and the energy is given by the equation:

$$E = \frac{m_l^2 \hbar^2}{2I}$$

where I is the moment of inertia of the particle.

2. The wavefunctions corresponding to the motion of a particle on the surface of a sphere are known as spherical harmonics. The mathematical form that they take depends upon two quantum numbers; the first is m_p and the second is the azimuthal quantum number l . The rotational kinetic energy of the particle is quantized according to the equation:

$$E = l(l+1) \frac{\hbar^2}{2I}$$

The angular momentum, L , is equal to $\hbar[l(l+1)]^{1/2}$ and the component of angular momentum in any particular direction, L_z (taken to be the z direction), is equal to $m_l \hbar$. The angular momentum in the x and y directions is unknown. This leads to “cones of uncertainty”, on which the angular momentum vector must lie.

3. The spherical harmonic wavefunctions can be applied to the rotational spectra of diatomic molecules, and also to electron and nuclear spin. In the latter case, the quantum numbers must be allowed to have half-integral values.

Problems

5.1. The wavefunction for a particle moving in a circle can be written as $\psi = N \sin \alpha \phi$, where N and α are constants and ϕ is the angle of rotation. Find the value of the normalization constant and the allowed values of the quantum number α . The following trigonometrical equation may be found useful:

$$\sin^2 \theta = \frac{1}{2} (1 - \cos 2\theta)$$

5.2. The equilibrium internuclear distance in ${}^1\text{H}{}^{35}\text{Cl}$ is 0.1275 nm. Calculate the difference in rotational energy between the $J = 0$ and $J = 1$ levels and the wavelength of radiation that will be absorbed in promoting the transition from $J = 0$ to $J = 1$. The masses of ${}^1\text{H}$ and ${}^{35}\text{Cl}$ are 1.008 and 34.97 amu, respectively.

5.3. Draw vector diagrams to represent the angular momentum of states with the following quantum numbers: (a) $l = 2, m_l = 2$; (b) $l = 1, m_l = 0$; (c) $s = \frac{1}{2}, m_s = -\frac{1}{2}$.

5.4. A sample of deuterium is placed in a magnetic field. Calculate the minimum angle to the field that can be adopted by the spin angular momentum vector of the deuterium nucleus.

Further Reading

P. A. Cox, *Introduction to Quantum Theory and Atomic Structure*, Oxford University Press, Oxford, 1996.

J. W. Linnett, *Wave Mechanics and Valency*, Methuen, London, 1960.

G. M. Barrow, *Physical Chemistry*, 6th edn., McGraw-Hill, New York, 1996, chap. 9.